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Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application conformes à la version described on the following page, as originally filed.

Les documents fixés à cette attestation sont initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

99204177.2

Der Präsident des Europäischen Patentamts; Im Auftrag

For the President of the European Patent Office Le Président de l'Office européen des brevets p.o.

I.L.C. HATTEN-HECKMAN

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## Blatt 2 der Bescheinigung Sheet 2 of the certificate Page 2 de l'attestation

Anmeldung Nr.:

Application no.: Demande n\*:

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Anmelder: Applicant(s): Demandeur(s):

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**NETHERLANDS** 

Bezeichnung der Erfindung: Title of the invention: Titre de l'invention:

Semiconductor device comprising a security coating smartcard provided therewith

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Semiconductor device comprising a security coating and smartcard provided therewith.

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The invention relates to a semiconductor device having a substrate, which is provided on a first side with a first semiconductor element and at least one security coating which comprises a powdery filler incorporated in a matrix.

The invention also relates to a smartcard provided with a semiconductor device comprising a memory and a security coating, which comprises a powdery first filler incorporated in a matrix.

From US-A 5,399,441 a semiconductor device of the type mentioned in the opening paragraph is known, in which the security coating is a layer having a matrix of silicon oxide in which a powdery filler is incorporated. When the matrix is filled with a filler, such as an oxide, a nitride or a carbide of silicon, aluminum or a metal, the coating inhibits at least 90% of the transmission of visible light. When the matrix is filled with an inorganic salt of a heavy metal, the coating inhibits at least 90% of the transmission of a specific type of infrared radiation.

A disadvantage of the known semiconductor device is that about 10% of the radiation of selected wavelengths is transmitted through the coating. With state-of-the art microscopes operated with visible light or near infrared radiation, this is too much to provide for adequate security. Personal or financial data contained in the known semiconductor device will be accessible and a method to change the data illegally might be found by reverse engineering of the semiconductor device. So if the known semiconductor device is applied in a smartcard and if the smart card falls into the hands of a dishonest person, the contained data will be vulnerable to a breach of security.

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It is therefore a first object of the invention to provide a semiconductor device of the type mentioned in the opening paragraph, in which the coating inhibits transmission of visible light and of near infrared radiation to a larger extent. It is a second object to provide a +31 EP992041772 JetFax M93

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smart card of the type mentioned in thoopening paragraph, of which the semiconductor device has the improved cating.

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The first object is achieved in that:

- 5 the difference of the refractive index of the powdery, first, filler and of the matrix is at least 0.3 and
  - the coating comprises a second filler, which is a substantial absorber of radiation with wavelengths at least in the range of 800 to 1400 nm and which is free of heavy metals.

The second filler is a material, which is for example present as particles and which transforms incident radiation into heat. As a substantial absorber of radiation, it absorbs the radiation for at least 99 per cent. The second filler absorbs the radiation to 1400 nm at least. Radiation with a wavelength larger than 1.4 µm need not to be absorbed as much as 99%, as the large wavelength itself hides details of the first semiconductor element in the semiconductor device of the invention. Preferably, the second filler absorbs the radiation with wavelengths in the range of 800 to 2000 nm. Suitable materials are for instance, titanium nitride and titanium oxynitride.

In a preferred embodiment, the second filler comprises titanium nitride. Due to the use of titanium nitride as a second filler an inhibition of the transmittance of at least 99.9 % of radiation with a wavelength between 600 and 2000 nm can be realized easily. The inventors have observed that particles of TiN in the coating can have a surface comprising TiO<sub>2</sub>, which is believed to follow from accidental oxidation. Such an oxidation occurs for example, when the security coating is applied in the manufacture of the semiconductor device from an acid, aqueous composition.

A first advantage of this second filler is that titanium nitride is known in the manufacture of semiconductor devices in cleanroom facilities. Moreover, it is free of heavy metals. This is an important advantage, as heavy metals are poisonous materials that are problematic during the production and after disposing the semiconductor device comprising the security coating as waste. A further advantage is that titanium nitride is commercially available in various particle size distributions.

The first filler present in the security coating of the device of the invention, operates by scattering visible light. Due to this, radiation in the visible spectrum as well as in the ultraviolet spectrum is inhibited by scattered reflection to penetrate. In order that the coating has sufficient scattering potential, it was found to be necessary that the difference of the refractive index of the first filler and that of the matrix is at least 0.3. As the refractive

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index of a matrix is generally in the order of 1.4-1.5, first fillers with a refractive index larger than 1.7-1.8 can be used. Examples of first fillers include oxides f zirconium, titanium, zinc, manganese, chromium, niobium, iron, nickel, strontium, yttrium, vanadium, gallium, copper and cobalt and nitrides of niobium, titanium and zirconium.

In a further embodiment, the first filler comprises titanium oxide. This material has a very high refractive index and provides therefore strong scattering of visible light and of radiation in the ultraviolet spectrum. If titanium nitride is used as the second filler, it is preferred to have a weight ratio of titanium oxide and titanium nitride present in the coating in the range of 0.25 to 4.

The amount of filler used in the coating of the semiconductor device of present invention can be varied over a wide range, depending, for example, on the electrical characteristics desired in the coating. Generally, the first and the second filler are present in a combined amount in the range of 10 to 90 per cent by weight of the coating. The first and the second filler are preferably present as particles with a size in the submicron range.

The material of the matrix of the coating can be chosen from several materials, such as a mono(metal)phosphate compound, wherein the metal is for example chosen from the group of zinc and aluminum, or a component prepared from a silica precursor resin. Such matrices are described, for example, in the non-pre-published application WO IB99/01007 and in US-A 5,399,441. Preferably monoaluminum phosphate is used for the matrix. Due to the use of this material, the security coating has a great mechanical strength and it has a good etch persistancy. Further on, the coating with monoaluminum phosphate can be readily provided in a thickness ranging from 1 to  $10 \, \mu m$ .

In a preferred embodiment the coating has a thickness in the range of 1 to 5 µm. It is especially preferred to have a coating thickness of less than 3 µm. The coating is nevertheless opaque to visible light and near infrared radiation. A first advantage is that the thickness of the semiconductor device is increased to a small degree only by the provision of the security coating. This is advantageous for the use of the semiconductor device of the invention in a smartcard, in which the device thickness is limited. A second advantage is that it is further possible to apply more than one coating in the semiconductor device. A third advantage is that the application of end-contacts in the manufacture of the semiconductor device is easier than with coatings with larger thicknesses. These end-contacts may be applied in a method comprising subsequently the steps of depositing a photoresist at regions, where end-contacts are desired; depositing and drying a composition comprising fillers incorporated in a matrix; removing the photoresist and the composition deposited thereon; heating, with

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which the security coating is formed; and applying an electrically well-conducting material, such as copper, at said regions. When the coating thickness is less than 5  $\mu$ m, the removal of the photoresist and the coating deposited thereon is made easier.

If desired, other materials may also be present in the coating. For instance, an agent which modifies the surface of the fillers for better adhesion or a dispersion agent may be used.

In a further embodiment, the semiconductor device of the invention comprises a light-sensitive element, which is covered by the security coating and which, after damaging of the security coating, reacts on exposure to visible light to induce a permanent change of state in the element containing data to be secured. Said reaction, which takes place in this embodiment after malicious damaging of the coating, can be electrically or chemically. As a result, the layout of selected parts of the semiconductor device, such as a layer comprising interconnect lines, is destroyed.

In another embodiment, the semiconductor device of the invention comprises a light-sensitive element and an electrically programmable element containing data to be secured, which are covered by the security coating and which light-sensitive element, after damaging of the coating, reacts on exposure to visible light to induce erasure of the data to be secured and to bring the electrically programmable element into a non-programmable state.

Said light-sensitive elements comprise for example resistors in combination with diodes or transistors, which are coupled to an output terminal, such as an amplifier. An example of a light-sensitive element is known for EP-A 0939 933. It comprises a biasing transistor arranged to provide a bias current; a reverse biased transistor having a conducting electrode electrode arranged to be reverse biased by said bias current and having a conducting electrode; and a resistor coupled between a supply voltage and said conducting electrode. Incident visible light is detected by a voltage drop at the conducting electrode of the reverse biased transistor, which can send a signal to the output. The output can induce resetting of an electrically erasable programmable random-access memory, known as EEPROM. The output can also induce a complete writing of an one-time electrically programmable random-access memory. Due to the complete writing erasure of the data to be secured takes place.

The substrate of the semiconductor device of the invention can be made from several materials. Suitable materials are for example silica, alumina and a polymer material such as polyimide. There are several materials and constructions, which can be used in the first semiconductor elem into of the semiconductor device of the invention. Known constructions are for example the MOS-field effect transistor and the bipolar transistor. Such construction can

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comprises memory units, as is known per se. Known materials comprise metals, inorganic semiconductors and organic conductors and semiconductors.

By preference, the semiconductor device is a vital part of a smart card, such as a cash card, a credit card or any other card. The expression "smart card" is meant to describe in general any portable apparatus, which comprises a semiconductor device that contains only data, which cannot be changed by the apparatus solely. Although the smart card is now a card-like apparatus, the introduction of contactless smartcards gives the opportunity of incorporating the function of the smart card into another apparatus, such as, for example, a electronic diary.

The second object of the invention is realized in that it comprises the semiconductor device of the invention. It is thereby protected against visual inspection from outside. By preference, the smart card comprises the semiconductor device of the invention provided with a light-sensitive element, so as to protect the memory of the smart card against visual inspection after opening of the semiconductor device.

These and other aspects of the semiconductor device of the invention will be apparent from and elucidated with reference to the embodiment described hereinafter, which constitute a non-limiting example.

In the drawings:

Fig. 1 is a diagrammatic, cross-sectional view of a semiconductor device in accordance with the invention.

Fig. 2 shows the chemical structure of a security coating on a substrate in accordance with the invention, and

Fig. 3 shows the transmission of radiation T in % by two security coatings A and B as a function of the wavelength  $\lambda$  between 400 and 2000 nm, of which coating B is according to the invention.

In Figure 1 the semiconductor device 20 has a substrate 1 of silica, having a first side 2. On the first side 2, the device 20 is provided with a first semiconductor element 3, which is in this exampl a bipolar transistor with an emitter region 4, a base region 5 and a collector region 6. Said regions 4,5 and 6 are provided in a first layer 7, which is covered with a patterned insulating layer 8 of silicon oxide. The insulating layer 8 is patterned such, that it

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has contact windows 9 and 10, at which a patterned conductive layer 11 of aluminum, contacts the emitter region 4 and the base region 5. A passivation layer 13 is situated on the first side 2. This passivation layer 13 is for example a layer of silicon oxide or silicon nitride. The first side 2 is further provided with a security coating 14 of the invention. Both the passivation layer 13 and the security coating 14 leave the conductive layer 11 free in the region 12, therewith forming a contact face so as to enable external contact.

In order to form the region 12, the passivation layer 13 has been patterned according to a known method. Subsequently, a photoresist has been deposited onto the passivation layer 13 at desired regions. These regions comprise, for example, the region 12 and regions at which the semiconductor device 20 is separated from a neighboring device manufactured at the same slice of silicon. Such regions are commonly referred to as scribe lines.

Then, a composition was prepared to spincoat on the passivation layer 13 of the substrate 1 of the semiconductor device 20. The composition comprised 50 grams of monoaluminum phosphate acidified with 50 grams of 0.01 M hydrochloric acid, a hydrolysis mixture of tetraethoxysilane (TEOS) comprising 5 grams of TEOS, 25 grams of TiO<sub>2</sub> and 25 grams of TiN. After wet ball milling overnight, the coating liquid was spincoated on the passivation layer 13 and on the conductive layer 11, which was covered by a photostructured polymer on contact faces and on sawlines. Subsequently, the so formed coating 14 was dried at 100°C and the photoresist was removed by means of ethanol. Then, the monoaluminum phosphate matrix was formed by heating the layer at a temperature in the range of 400-500°.

For the sake of simplicity, only the first semiconductor element 3 is shown, but in practice the first layer 7 generally comprises a plurality of such elements, and the conductive layer 11 comprises a number of layers and, in addition, is provided with many connection faces for external contact. The assembly may form an integrated circuit. As known to those skilled in the art, field effect transistors can be present instead of or besides the bipolar transistor. As further known to those skilled in the art, other elements, such as capacitors, resistors and diodes can be integrated in the semiconductor device 20.

In Figure 2 a security coating 14 in accordance with the invention is present on the passivation layer 13. The matrix of the coating 14 comprises molecules of a first material, in this case monoaluminum phosphate Al(OPO<sub>3</sub>H<sub>2</sub>)<sub>3</sub>, which molecules are bonded to the surface of the passivation layer and to each other. The bonds are formed by condensation of hydroxylgroups. In order to clarify the m lecular process of bonding, Figure 2 shows the molecules of the matrix and the particles which act as first or second filler in a transition state

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to bonding. In this state the coating has an internal structure as in the bonded state, but there has not yet taken plac any condensation. The encircled pairs of hydroxylgroups must be understood to change on bonding in an oxygen bond and in a liberated  $H_2O$  molecule. The matrix further comprises particles of  $TiO_2$  en TiN, which act as the first and second filler in the matrix. The particles preferably have an average particle size between 50 nm and 1  $\mu$ m. The TiN-particles have a oxidized surface, e.g. their surface mainly comprises  $TiO_2$  and they can be bonded to the matrix as easily as the  $TiO_2$ -particles.

In Figure 3 the transmission T in % of radiation by two different security coatings A and B as a function of the wavelength  $\lambda$  between 400 and 2000 nm is shown. The first coating A, not according to the invention, consisted of about 55 weight per cent of monoaluminum phosphate, about 40 weight per cent of particles of TiO<sub>2</sub> as the first filler and about 5 weight per cent of tetraethoxysiloxane. The coating A had a thickness of 4  $\mu$ m. Whereas the transmission is very low in the range from 400 to 600 nm, the transmission increases up to 50 per cent at about 1300 nm and to 75 per cent at about 2000 nm.

The second line, indicated as B, shows the transmission by a security coating of the invention, consisting of about 48 weight per cent monoaluminum phosphate, about 24 weight per cent of particles of TiO<sub>2</sub>, about 24 weight per cent of particles of TiN and about 4 weight per cent of tetraethoxysiloxane. Clearly, the transmission is inhibited in the spectrum from 400 to 2000 nm for a very large part, e.g. for more than 99.99 per cent. Therefore, the invention provides an excellent security coating, which certainly improves the known security coating and with which data can be secured well.

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CLAIMS:

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- 1. A semiconductor device (20) having a substrate (1) which is provided on a first side (2) with a first semiconductor element (3) and at least one security coating (14) which comprises a powdery filler incorporated in a matrix, characterized in that
- the difference of the refractive index of the powdery, first, filler and of the matrix is at least 0.3 and
- the coating comprises a second filler, which is a substantial absorber of radiation with wavelengths at least in the range of 800 to 1400 nm and which is free of heavy metals.
- 2. A semiconductor device (20) as claimed in Claim 1, characterized in that the second filler comprises TiN.
  - 3. A semiconductor device (20) as claimed in Claim 1 or 2, characterized in that the first filler comprises TiO<sub>2</sub>.
- 4. A semiconductor device (20) as claimed in Claim 1, characterized in that the matrix of the security coating comprises monoaluminumphosphate.
  - 5. A semiconductor device (20) as claimed in Claim 4, characterized in that the security coating has a thickness less than 3 µm.
  - 6. A semiconductor device (20) as claimed in Claim 1, characterized in that a light-sensitive element and an element containing data are present, which are covered by the security coating (14) and which light-sensitive element, after damaging of the coating, reacts on exposure to visible light to induce a permanent change of state in the element containing data.
  - 7. A semiconductor device (20) as claimed in Claim 1, characterized in that a light-sensitive element and an electrically programmable element containing data are present, which are covered by the security coating (14) and which light-sensitive element, after

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damaging of the coating, reacts on exposure to visible light to induce erasure of the data and to bring the electrically programmable element into a non-programmable state.

- 8. A smartcard provided with a semiconductor device (20) comprising a memory and a security coating (14), which comprises a powdery first filler incorporated in a matrix, characterized in that
  - the coating comprises a second filler, which is an absorber of radiation with a wavelength in the range of 800 and 1400 nm and
  - the difference of the refractive index of the first filler and of the matrix is at least 0.3.

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ABSTRACT:

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A semiconductor device (20) comprising a substrate (1) is provided with a first semiconductor element (3) on a first side (2), and a security coating (14) comprising a matrix, a first filler and a second filler. The second filler is an absorber of radiation with a wavelength between 800 and 1400 nm and the refractive index of the first filler differs with at least 0.3 from the refractive index of the matrix. As a result, the security coating inhibits transmission of radiation with a wavelength between 400 and 1400 nm for a very large extent. The semiconductor device (20) can be incorporated in a smartcard.

Fig. 1

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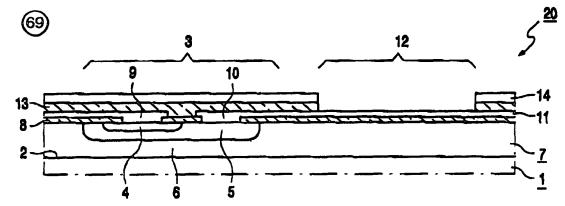


FIG. 1

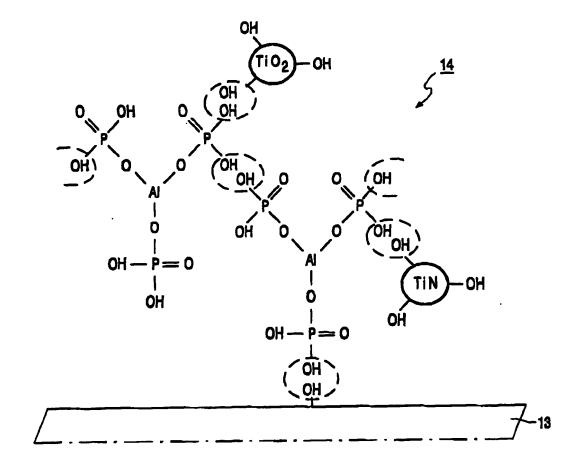


FIG. 2

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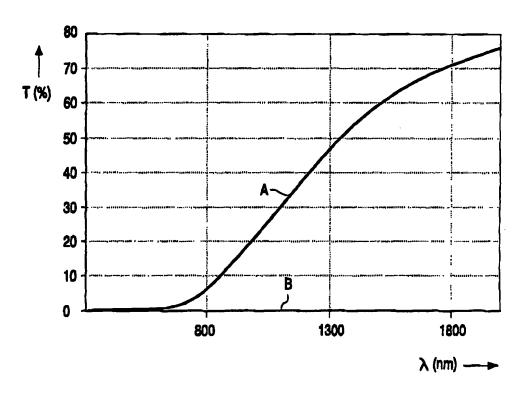


FIG. 3